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## (54) Back-print recording medium for ink-jet printing

(57) A back print recording medium is provided which can realize a high-definition, high-resolution image The back print recording medium (1) comprises: a transparent substrate (2); and an ink receptive layer (3) and a light diffusing, ink permeable layer (4) provided in that order on the transparent substrate (2), wherein a dot of a ink droplet (5) is formed in the ink receptive layer (3) and the diameter of the printed dot viewed through the transparent substrate is smaller than that of the printed dot viewed through the light diffusing ink permeable layer.

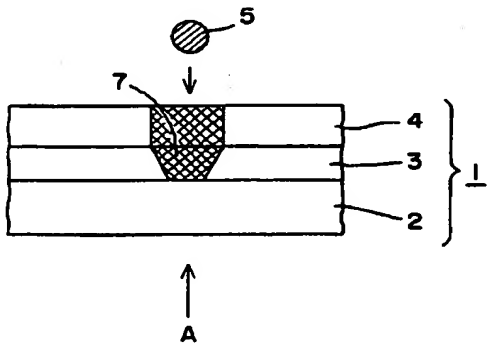


FIG. 1

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**Descripti n**

## BACKGROUND OF THE INVENTION

### Field of the Invention

The present invention relates to the so-called "back print recording medium" wherein an ink composition is applied to one side of the medium and the image formed by the ink composition is viewed through the other side of the medium.

### Background Art

A recording medium called "back print recording medium" wherein an ink composition is applied to one side of the medium and the image formed by the ink composition is viewed through the other side of the medium is known in the art. Such a recording medium basically comprises a transparent substrate bearing an ink receptive layer for absorbing and fixing an ink composition and a light diffusing, ink permeable layer composed mainly of silica. Printing is performed from the ink permeable layer side, for example, by ink jet recording. The ink is passed through the ink permeable layer and reaches the ink receptive layer. The formed ink image is viewed through the transparent layer with the aid of reflected light or transmitted light through the transparent substrate side. By virtue of gloss and smoothness of the transparent substrate, the viewed printed image has a good texture. Therefore, the back print recording medium has been utilized in printing of an image which is desired to give an impression of high quality.

On the other hand, recording media comprising an ink receptive layer formed of a polyvinyl acetal resin are described, for example, in Japanese Patent Laid-Open Nos. 219042/1994 and 72390/1996 and Japanese Patent Publication No. 23597/1993. To the best of the inventor's knowledge, the polyvinyl acetal resin, however, has not been applied to the ink receptive layer of the back print recording medium.

## SUMMARY OF THE INVENTION

The present inventors have now found that, in the so-called "back print recording medium," a good image can be yielded by rendering the dot diameter of a printed image viewed through the transparent substrate smaller than the dot diameter of the printed image viewed through the light diffusing, ink permeable layer. The present invention has been made based on such finding.

Accordingly, an object of the present invention is to provide a back print recording medium which can realize a good image.

According to one aspect of the present invention, there is provided a recording medium comprising: a transparent substrate; an ink receptive layer and a light diffusing, ink permeable layer provided in that order on the transparent substrate, said recording medium permitting printing to be performed from the light diffusing, ink permeable layer side and, in addition, the print to be viewed through the transparent substrate,

the diameter of the printed dot viewed through the transparent substrate being smaller than that of the printed dot viewed through the light diffusing, ink permeable layer.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view, partly in section, of one embodiment of the recording medium according to the present invention, that is, a recording medium 1 comprising a transparent substrate 2 and an ink receptive layer 3 and a light diffusing, ink permeable layer 4 provided in that order on the transparent substrate 2, wherein recording is performed by an ink droplet 5 on a recording medium 1 from the layer 4 side and, for a dot 7, as an element of an image, constituted by an ink droplet 5 in the ink receptive layer 3, the diameter of the dot viewed through the transparent substrate 2, that is, from a direction indicated by an arrow A, is smaller than that of the dot viewed through the light diffusing, ink permeable layer 4; and

Fig. 2 is a diagram showing the state of an image recorded on one embodiment of the recording medium according to the present invention, wherein Fig. 2 (a) is a diagram showing the state of an ink droplet 5 being printed by ink jet recording from the layer 4 side of a recording medium 1 comprising a transparent substrate 2 and an ink receptive layer 3 and a light diffusing, ink permeable layer 4 provided in that order on the transparent substrate 2, Fig. 2 (b) shows the state of the ink droplet 5 being deposited onto the layer 4 and penetrating the layer 4 toward the ink receptive layer 3, Fig. 2 (c) is a diagram showing such a state that an ink composition 6 then reaches the ink receptive layer 3 and penetrates the ink receptive layer 3 while reducing the diameter of the dot, and Fig. 2 (d) is a diagram showing the state of a major part of the ink composition 6 finally reaching the ink receptive layer 3 to form one dot as an element of an image.

## DETAILED DESCRIPTION OF THE INVENTION

The recording medium according to the present invention comprises: a transparent substrate; and an ink receptive layer and a light diffusing, ink permeable layer provided in that order on the transparent substrate. In this recording medium, printing is performed through the light diffusing, ink permeable layer, while the printed image is viewed through the transparent substrate.

A preferred embodiment of the recording medium according to the present invention is shown in Fig. 1. In the drawing, a recording medium 1 comprises a transparent substrate 2 and an ink receptive layer 3 and a light diffusing, ink permeable layer 4 provided in that order on the transparent substrate 2. In this recording medium, recording is performed through the layer 4 by means of an ink droplet 5. Preferably, the recording is performed by ink jet recording. In the recording medium of the present invention, a dot 7, as an element of an image, formed by the ink droplet 5 takes a form, in the ink receptive layer 3, as shown in Fig. 1. In particular, the diameter of the dot viewed through the transparent substrate (from a direction indicated by an arrow A) is smaller than that of the dot viewed through the light diffusing, ink permeable layer. In the present invention, the diameters of the dots may be compared in terms of the equivalent circular diameter.

When the dot takes such a form, an image having better quality can be realized. In particular, high-definition, high-resolution recording is possible. In particular, according to the present invention, creation of a particulate spot often observed in an image printed by ink jet recording can be effectively inhibited, making it possible to realize a printed image having quality comparable to a photograph. The printed image has a further advantage that a good image can be observed through both reflected light and transmitted light. Further, the water resistance and the storage stability are also good, and stickiness after the printing can be reduced. Furthermore, advantages inherent in the back print, such as good gloss and excellent scratch resistance of the printed image, are of course offered.

The state of an image being recorded on the recording medium according to the present invention will be described in more detail with reference to Fig. 2. Fig. 2 (a) is a diagram showing the state of an ink droplet 5 being printed by ink jet recording from a light diffusing, ink permeable layer 4 side of a recording medium 1 comprising a transparent substrate 2 and an ink receptive layer 3 and a light diffusing, ink permeable layer 4 provided in that order on the transparent substrate 2. Upon deposition onto the layer 4, as shown in Fig. 2 (b), the ink droplet 5 penetrates the layer 4 toward the ink receptive layer 3. During permeation into the layer 4, the ink composition 6 may penetrate while increasing or reducing the dot diameter. However, penetration of the ink dot without changing the diameter is preferred. Thereafter, the ink composition 6 reaches the ink receptive layer 3. During the permeation into the ink receptive layer 3, as shown in Fig. 2 (c), the ink composition 6 penetrates while reducing the dot diameter. Finally, a major part of the ink composition 6 reaches the ink receptive layer 3 to form one dot as an element of an image. As shown in Fig. 2 (d), the form of the dot is such that the diameter of the dot viewed through the transparent substrate is smaller than that of the dot viewed through the light diffusing, ink permeable layer. As shown in the drawing, depending upon the amount of the ink composition printed, the ink composition does not penetrate to reach the boundary between the ink receptive layer 3 and the transparent substrate 2, and the penetration of the ink composition is stopped within the ink receptive layer 3. This embodiment also falls within the scope of the present invention so far as the diameter of the dot viewed through the transparent substrate is smaller than that of the dot viewed through the light diffusing, ink permeable layer.

According to a preferred embodiment of the present invention, the above dot form can be realized in an ink receptive layer comprising a polyvinyl acetal resin. Therefore, according to the present invention, there is provided a recording medium comprising an ink receptive layer containing a polyvinyl acetal resin.

According to a preferred embodiment of the present invention, the degree of acetylization is preferably about 2 to 20% by mole, more preferably about 5 to 15% by mole. When the degree of acetylization of the polyvinyl acetal falls within the above range, it is possible to provide an ink receptive layer which enables a dot having high transparency and circularity to be formed. Further, the adhesion of the ink receptive layer to the substrate is advantageously excellent. An additional advantage of the ink receptive layer is such that excellent waterproofness, ink fixation, and storage stability of the image (particularly causing neither feathering nor bleeding in an high-humidity environment) can be offered while enjoying high ink absorption rate and large ink absorption. Furthermore, the above ink receptive layer can effectively prevent color-to-color intermixing problem called "bleeding" in the color printing. Further, interestingly, use of the polyvinyl acetal as the ink receptive layer can advantageously effectively prevent cracking which is likely to be created in the formation of the light diffusing, ink permeable layer on the ink receptive layer, especially during drying.

The polyvinyl acetal resin used in the present invention can be prepared by reacting polyvinyl alcohol with an aldehyde to conduct acetylization. It may be prepared also by using polyvinyl acetate as the starting compound to conduct saponification and acetalization. The acetalization may be performed by any conventional method, such as a dissolution method, a precipitation method, or a method using a homogeneous system.

The above polyvinyl alcohol is not particularly limited. In general, however, the degree of polymerization is preferably about 300 to 4500, more preferably 500 to 4500. Use of a polyvinyl acetal resin prepared from polyvinyl alcohol having a high degree of polymerization is likely to provide an ink receptive layer having good ink fixation and

waterproofness. Although the degree of saponification of the polyvinyl alcohol is also not particularly limited, it is preferably about 80.0 to 99.5% by mole.

Examples of aldehydes usable for condensation with the polyvinyl alcohol include aliphatic aldehydes, such as formaldehyde, acetaldehyde, butyl aldehyde, hexyl aldehyde, octyl aldehyde, and decyl aldehyde; benzaldehyde, 2-methylbenzaldehyde, 3-methylbenzaldehyde, 4-methylbenzaldehyde, and other alkyl-substituted benzaldehydes and chlorobenzaldehyde and other halogen-substituted benzaldehydes; aromatic aldehydes, such as phenyl acetaldehyde, β-phenyl propionaldehyde, and other phenyl-substituted alkyl aldehydes; and aromatic aldehydes with substituents, such as hydroxy, alkoxy, amino, and cyano groups, in the aromatic ring. It is also possible to use aldehydes having a condensed aromatic ring, such as naphthaldehyde and anthraldehyde.

Use of a polyvinyl acetal resin prepared from an aromatic aldehyde can provide an ink receptive layer having excellent ink fixation, waterproofness, and transparency.

The degree of acetylization in the polyvinyl acetal resin used in the present invention is preferably in the range of from about 2 to 20% by mole, more preferably about 5 to 15% by mole, most preferably about 7 to 10% by mole. Use of the resin having a degree of acetylization in the above range can provide an ink receptive layer having excellent ink fixation and waterproofness.

In the present invention, commercially available polyvinyl acetal resins may also be used, and specific examples thereof include S-lec KX-1 (degree of acetalization: 8 % by mole) and KW-1 (degree of acetalization: 9 % by mole) (both products being manufactured by Sekisui Chemical Co., Ltd.).

The ink receptive layer in the recording medium according to the present invention may be formed as a coating of the above polyvinyl acetal resin on the transparent substrate. More specifically, it may be formed by providing a solution of the above polyvinyl alcohol resin in a suitable solvent (for example, a mixed solvent composed of water and isopropyl alcohol), coating the solution onto a substrate, and drying the coating. The coating may be performed by conventional means, for example, by using a roll coater, an air knife coater, a blade coater, a rod coater, a bar coater, or a Komma coater.

The ink receptive layer in the recording medium according to the present invention may comprise, in addition to the polyvinyl acetal resin, other water-soluble resin(s), a water-proofing agent, a surfactant, a preservative, an ultraviolet absorber and the like.

In the recording medium according to the present invention, the thickness of the ink receptive layer may be suitably determined by taking into consideration properties required of the recording medium. However, it is preferably about 3 to 15 μm, more preferably about 5 to 10 μm.

Materials usable for the transparent substrate in the recording medium according to the present invention include poly ster resin, polyolefin resin, polystyrene resin, and polyvinyl chloride resin. In general, the thickness of the transparent substrate is preferably about 50 to 300 μm from the viewpoint of the carriability of the recording medium through a printer and the like. According to a preferred embodiment of the present invention, the transparent substrate in its surface which comes into contact with the ink receptive layer has been subjected to adhesion-imparting treatment. This treatment can improve the adhesion between the transparent substrate and the ink receptive layer. This adhesion-imparting treatment may be performed by a conventional method. Specific examples thereof include corona discharge treatment of the surface of the substrate and coating of a solution or emulsion of an acrylic, polyester, or urethane resin onto the substrate to a thickness of not more than about several μm. According to another preferred embodiment of the present invention, the surface of the transparent substrate on which the ink receptive layer is not provided has been subjected to antistatic treatment. This treatment can effectively prevent sticking of recording media against each other caused by static electricity. The antistatic treatment may be performed by any conventional method. In particular, it may be performed, for example, by adding a surfactant having an antistatic property to a resin solution or a resin emulsion and coating the mixture onto the substrate. More specifically, a treatment which can bring the surface resistance to not more than $1 \times 10^{15}$ Ω, preferably not more than $1 \times 10^{13}$ Ω, suffices for the antistatic treatment. Further, a desired pattern, for example, a network pattern, may be provided on the surface of the substrate, and the surface of the substrate may b subjected to gloss-imparting treatment.

The light diffusing, ink permeable layer in the recording medium according to the present invention may be generally constructed so as to be utilized as a light diffusing, ink permeable layer in a back print recording medium. For example, it may comprise a binder resin, a whitening agent, a porous material and the like. According to a preferred embodiment of the present invention, the light diffusing, ink permeable layer may comprise at least a carboxyl-modified polyvinyl alcohol, colloidal silica, a whitening agent, and a synthetic silica. Utilization of the carboxyl-modified polyvinyl alcohol is preferred from the viewpoint of markedly improving the storage stability of the printed image. The carboxyl-modified polyvinyl alcohol may also be a commercially available one, and examples thereof include those available as Gosenal T series from Nippon Synthetic Chemical Industry Co., Ltd., such as Gosenal T-215, 230, 330, 350, and 330H. The colloidal silica referred to herein is usually an anionic colloidal dispersion prepared by stably dispersing ultrafine particles of silicic acid anhydride (silica) and may be prepared, for example, by the following method. At the outset, an aqueous sodium silicate solution is passed into a cation exchange resin to prepare a sol having an $SiO_2/Na_2O$ ratio of

60 to 130. Subsequently, the sol is heated and fired at a temperature of 60°C or above to grow into discrete dispersed particles, and a sol passed through an ion exchange resin layer is added thereto to cause polymerization deposition. Thus, colloidal silica can be prepared as a sol which has been grown into particles having an average particle diameter of 3 to 200 nm and stabilized. Further, in the present invention, commercially available colloidal silica may be used, and examples thereof include Ludox manufactured by Du Pont, Syton manufactured by Monsanto, Nalcoag manufactured by Nalco, and Snowtex manufactured by Nissan Chemical Industry Ltd. Whitening agents usable in the present invention include, for example, titanium oxide, white fluorescent pigments, and fluorescent dyes. The brightness of the recording medium according to the present invention may be suitably determined by taking into consideration the ink permeability, ink absorption and the like. Commercially available whitening agents may also be used, and examples thereof include Whitex (manufactured by Sumitomo Chemical Co., Ltd.), a fluorescent dye.

According to a preferred embodiment of the present invention, the light diffusing, ink receptive layer comprises a synthetic silica. This is because addition of this synthetic silica results in improved ink permeability. The particle diameter, pore volume, and average pore diameter of the synthetic silica may be suitably determined by taking into consideration the ink absorption and the ink permeability. The synthetic silica may also be commercially available one, and examples thereof include Mizukasil and Mizukasoap (manufactured by Mizusawa Industrial Chemicals Ltd.), FINESIL, Tokusil, Reolosil, and Excelica (manufactured by TOKUYAMA Corp.), Sylysia (Fuji Sylysia Chemical Ltd.), and Aerosil (manufactured by Nippon Aerosil Co., Ltd.).

In the recording medium according to the present invention, the thickness of the light diffusing, ink permeable layer is preferably about 15 to 40 μm, more preferably about 20 to 35 μm.

This light diffusing, ink permeable layer may be formed by dissolving or dispersing the above ingredients in a suitable solvent to prepare a coating liquid, coating the coating liquid onto the ink receptive layer formed on the transparent substrate, and drying the coating. The coating may be performed by conventional means, for example, by using a roll coater, an air knife coater, a blade coater, a rod coater, a bar coater, or a Komma coater.

Combination of the light diffusing, ink permeable layer having the above composition with the ink receptive layer comprising the polyvinyl acetal resin can provide a recording medium, having a good balance between ink absorption and ink permeability, which can realize high-definition, high resolution recording.

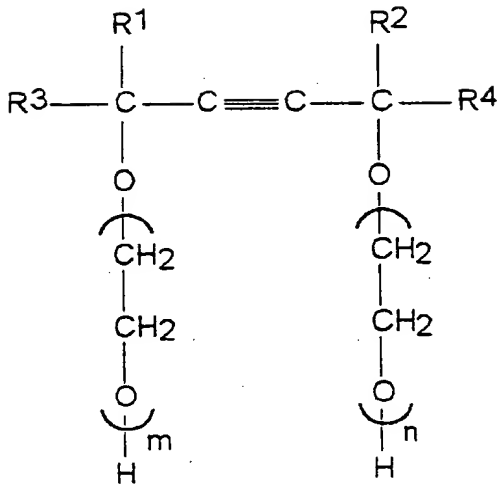
According to a preferred embodiment of the present invention, the total light transmittance of the recording medium according to the present invention is preferably about 20 to 80%, more preferably about 30 to 70%. The total light transmittance referred to herein means one determined by method B specified in JIS K 7105. In particular, the total light transmittance may be expressed in terms of the percentage of the quantity of transmitted light (T2) in the quantity of exposed light (T1), that is, (T2/T1) x 100 .

Further, according to a preferred embodiment of the present invention, the brightness of the recording medium viewed through the transparent substrate in the recording medium according to the present invention is preferably 50 to 90° , more preferably not less than 70° . The brightness referred to herein means brightness by Hunter specified in JIS P 8123 or ISO brightness specified in JIS P 8148.

The recording medium of the present invention is used for recording methods using an ink composition. Recording methods using an ink composition include, for example, ink jet recording, recording using writing implements, such as pens, and other various printing methods. Further, the ink composition is not limited to a liquid ink and embraces a wide variety of ink compositions such as solid colorants and colorants which, in use, are melted. In particular, the recording medium of the present invention is preferably used for ink jet recording. In particular, preferably, the recording medium of the present invention is used in a recording method involving the steps of ejecting droplets of the ink composition and depositing the ink droplets onto the recording medium.

Further, according to a preferred embodiment of the present invention, the ink composition used comprises at least a colorant, an organic solvent, water, and a surfactant. In particular, printing using an ink composition having penetrability enhanced by a surfactant into the recording medium can realize an image having higher density and better quality. Examples of preferred surfactants include acethylene glycols and anionic surfactants having a polyoxyethylene group.

Specific examples of preferred acetylene glycols include compounds represented by the following formula (I):



(I)

wherein $0 \leqq m + n \leqq 50$ and $R^1$, $R^2$, $R^3$, and $R^4$ each independently represent an alkyl group.

Specific examples of compounds represented by the formula (I) include Olfine Y, Surfynol 82, Surfynol 440, Surfynol 465, and Surfynol 485 (available from Air Products and Chemicals, Inc.). They may be added alone or as a mixture of two or more.

A anionic surfactants having a polyoxyethylene group include polyoxyethylene alkyl ether sulfates, polyoxyethylene alkylphenyl ether sulfates, polyoxyethylene styrenated phenyl ether sulfates, polyoxyethylene alkyl ether phosphates, and polyoxyethylene alkylphenyl ether phosphates. Among them, polyoxyethylene alkyl ether sulfates and polyoxyethylene alkylphenyl ether sulfates are preferred. In the anionic surfactant having a polyoxyethylene group, preferred counter ions for forming salts include inorganic ions, such as potassium, sodium, and ammonium ions, and amines, such as monoethanolamine and diethanolamine with ammonium ion being especially preferred.

The ink composition referred to herein means a black ink composition in the case of monochrome printing and a color ink composition in the case of color printing, specifically a yellow ink composition, a magenta ink composition, and a cyan ink composition and optionally a black ink composition. Further, the recording medium according to the present invention may also be used for recording using six ink compositions in total, that is, a yellow ink composition, two magenta ink compositions different from each other in color density, two cyan ink compositions different from each other in color density, and a black ink composition. Combination of the above ink compositions of six colors with the recording medium according to the present invention can realize a printed image with excellent gradation, free from any particulate spot and having a quality comparable to a photograph.

The colorant contained in the ink composition may be either a dye or a pigment.

Dyes usable herein include various dyes commonly used for ink jet recording, such as direct dyes, acid dyes, foodstuff dyes, basic dyes, reactive dyes, disperse dyes, vat dyes, soluble vat dyes, and reactive disperse dyes.

Regarding the pigment, inorganic and organic pigments are usable without any particular limitation. Examples of the inorganic pigment include, in addition to titanium oxide and iron oxide, carbon blacks produced by known processes, such as contact, furnace, and thermal processes. Examples of the organic pigment include azo pigments (including azo lake, insoluble azo pigment, condensed azo pigment, and chelate azo pigment), polycyclic pigments (for example, phthalocyanine, perylene, perinone, anthraquinone, quinacridone, dioxazine, thioindigo, isoindolinone, and quinophthalone pigments), dye chelates (for example, basic dye chelates and acid dye chelates), nitro pigments, nitroso pigments, and aniline black.

According to a preferred embodiment of the present invention, the above pigment is preferably added, to the ink, in the form of a pigment dispersion prepared by dispersing the pigment in an aqueous medium with the aid of a dispersant or a surfactant. Preferred dispersants include those which is commonly used or will be commonly used in the preparation of a dispersion of a pigment, for example, polymeric dispersant. In this connection, that the dispersant and the surfactant contained in the pigment dispersion function also respectively as the dispersant and the surfactant of the ink composition would be apparent to a person having ordinary skill in the art.

The amount of the pigment added to the ink is preferably about 0.5 to 25% by weight, more preferably about 2 to 15% by weight.

According to a preferred embodiment of the present invention, the ink composition used in the present invention

may further contain a wetting agent comprising a high-boiling organic solvent. Preferred examples of high-boiling organic solvents usable herein include polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, propylene glycol, butylene glycol, 1,2,6-hexanetriol, thiodiglycol, hexyleneglycol, glycerin, trimethylolethane, and trimethylolpropane; alkyl ethers of polyhydric alcohols, such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, and triethylene glycol monobutyl ether; urea; 2-pyrrolidone; N-methyl-2-pyrrolidone; 1,3-dimethyl-2-imidazolidinone; and triethanolamine.

The amount of the wetting agent added is preferably in the range of from 0.5 to 40% by weight, more preferably in the range of from 2 to 20% by weight, based on the ink.

Dispersants, surfactants, ultraviolet absorbers, and other additives, such as pH adjustors, preservatives, and antimolds, may be added to the ink composition used for recording onto the recording medium according to the present invention.

For the recording medium according to the present invention, recording may be performed using the ink composition in the same manner as used in the conventional back print recording medium. Further, according to a preferred embodiment of the present invention, provision of a protective layer on the light diffusing, ink permeable layer after recording of an image is preferred from the viewpoint of improving the storage stability. This protective layer can function to protect the recording medium against moisture, water, light, ozone and the like. In particular, the recording medium may be covered with a film or a synthetic paper, having low moisture permeability, with an ultraviolet absorber, an antioxidant, or a quenching agent incorporated therein. Alternatively, this film or synthetic paper may be applied to th recording medium with the aid of a pressure sensitive adhesive, or the film may be laminated onto the recording medium. Furthermore, provision of a pressure sensitive adhesive on the protective layer permits the recording medium per se to be applied onto the protective layer.

## EXAMPLES

The present invention will be described in more detail with reference to the following examples, though it is not limited to these examples only.

### Example 1

An ink receptive layer was formed on a substrate as follows. A 100 μm-thick polyethylene terephthalate film, one side of which had been subjected to adhesion-imparting treatment by coating with a dispersion of a polyester in water, was provided as the substrate. A polyvinyl acetal resin (KX-1, solid content 8%, degree of acetalization 8% by mole, composition of solvent: isopropyl alcohol/water = 40/60, manufactured by Sekisui Chemical Co., Ltd.) was dissolved in an isopropyl alcohol/water mixed solvent to a concentration of 7% to prepare a coating liquid. The coating liquid was coated by means of an applicator on the substrate on its side subjected to the adhesion-imparting treatment, the coating was dried in a drier kept at a constant temperature of 100°C for 2 min, thereby forming a 7 μm-thick ink receptive layer.

A light diffusing, ink permeable layer was then formed on the ink receptive layer as follows. At the outset, the following ingredients were mixed together to prepare a homogeneously dispersed coating liquid.

| | |
|---|---|
| Carboxyl-modified polyvinyl alcohol resin (anionic, degree of saponification 99% by mole or more, degree of polymerization 2200, T-330H, manufactured by Nippon Synthetic Chemical Industry Co., Ltd.) | 4.5 wt% |
| Silica (Sylysia 446, average particle diameter 4.5 μm, manufactured by Fuji Sylysia Ltd.) | 12 wt% |
| Titanium oxide (average particle diameter 0.26 μm) | 2 wt% |
| Fluorescent pigment (manufactured by Sinloihi Co., ltd.) | 2 wt% |
| Colloidal silica (Snowtex C, anionic, $SiO_2$ content 20%) | 10 wt% |
| Isopropyl alcohol/water = 40/60 mixed solution | Balance |

The coating liquid was coated by means of an applicator onto the ink receptive layer, and the coating was then dried in a drier kept at a constant temperature of 110°C for 3 min to form a 25 μm-thick light diffusing, ink permeable layer, thereby preparing a back print recording medium.

ple 2

A back print recording medium was prepared in the same manner as in Example 1, except that the amount of the coating liquid was regulated to a light diffusing, ink permeable layer thickness of 15 μm.

Example 3

A back print recording medium was prepared in the same manner as in Example 1, except that the amount of the coating liquid was regulated to a light diffusing, ink permeable layer thickness of 35 μm.

Comparative Example 1

A back print recording medium was prepared in the same manner as in Example 1, except that polyvinyl alcohol (PVA-117, manufactured by Kuraray Co., Ltd.) was used instead of the polyvinyl acetal resin to form the ink receptive layer.

Preparation of ink composition

The following ingredients were mixed together to prepare ink compositions

Ink set 1

| Yellow ink | |
|---|---|
| C.I. Direct Yellow 86 | 1.5 wt% |
| C.I. Direct Yellow 23 | 1.5 wt% |
| Diethylene glycol monobutyl ether | 10 wt% |
| Surfynol TG | 0.8 wt% |
| Diethylene glycol | 20 wt% |
| Triethanolamine | 0.2 wt% |
| Ion-exchanged water | 66 wt% |

| Cyan ink | |
|---|---|
| C.I. Direct Blue 199 | 3 wt% |
| Diethylene glycol monobutyl ether | 10 wt% |
| Surfynol TG | 0.8 wt% |
| Diethylene glycol | 20 wt% |
| Triethanolamine | 0.2 wt% |
| Ion-exchanged water | 66 wt% |

| Magenta ink | |
|---|---|
| C.I. Reactive Red 147 | 3 wt% |
| Diethylene glycol monobutyl ether | 10 wt% |
| Surfynol TG | 0.8 wt% |
| Diethylene glycol | 20 wt% |
| Triethanolamine | 0.2 wt% |
| Ion-exchanged water | 66 wt% |

| Black ink | |
|---|---|
| C.I. Direct Black 168 | 3 wt% |
| Diethylene glycol monobutyl ether | 10 wt% |
| Surfynol TG | 0.8 wt% |
| Diethylene glycol | 20 wt% |
| Triethanolamine | 0.2 wt% |
| Ion-exchanged water | 66 wt% |

All the above inks had a surface tension of about 30 mN/m, a viscosity of 4 mPa.s, and a pH value of about 9.

Ink set 2

| Yellow ink | |
|---|---|
| C.I. Pigment Yellow 17 | 3 wt% |
| Styrene/acrylic resin emulsion (solid content 30%) | 3 wt% |
| Maltitol | 10 wt% |
| Glycerin | 10 wt% |
| Triethanolamine | 1 wt% |
| 2-Pyrrolidone | 2 wt% |
| Ammonium polyoxyethylene alkyl ether sulfate | 0.8 wt% |
| Ion-exchanged water | 70.2 wt% |

| Magenta ink | |
|---|---|
| C.I. Pigment Red 122 | 3 wt% |

(continued)

| Magenta ink | |
|---|---|
| Styrene/acrylic resin emulsion (solid content 30%) | 3 wt% |
| Maltitol | 10 wt% |
| Glycerin | 10 wt% |
| Triethanolamine | 1 wt% |
| 2-Pyrrolidone | 2 wt% |
| Ammonium polyoxyethylene alkyl ether sulfate | 0.8 wt% |
| Ion-exchanged water | 70.2 wt% |

| Cyan ink | |
|---|---|
| C.I. Pigment Blue 15 : 3 | 3 wt% |
| Styrene/acrylic resin emulsion (solid content 30%) | 3 wt% |
| Maltitol | 10 wt% |
| Glycerin | 10 wt% |
| Triethanolamine | 1 wt% |
| 2-Pyrrolidone | 2 wt% |
| Ammonium polyoxyethylene phenyl ether sulfate | 0.8 wt% |
| Ion-exchanged water | 70.2 wt% |

| Black ink | |
|---|---|
| C.I. Pigment Black 7 | 3 wt% |
| Styrene/acrylic resin emulsion (solid content 30%) | 3 wt% |
| Maltitol | 10 wt% |
| Glycerin | 10 wt% |
| Triethanolamine | 1 wt% |
| 2-Pyrrolidone | 2 wt% |
| Ammonium polyoxyethylene alkyl ether sulfate | 0.8 wt% |
| Ion-exchanged water | 70.2 wt% |

All the above inks had a surface tension of about 35 mN/m, a viscosity of 3 mPa.s, and a pH value of about 9.5.

Ink set 3

A cyan ink and a magenta ink each of which the colorant concentration was one-fourth that of the cyan ink and the magenta ink in the ink set 1 were provided respectively as a light-colored cyan ink and a light-colored magenta ink. Thus, six ink sets in total were prepared.

Print evaluation test

Ink sets prepared above were used to print images on the back print recording media of Examples 1 to 3 and Comparative Example 1, and the printed images were evaluated as follows. In this case, for the ink sets 1 and 2, printing was performed using a color ink jet printer MJ910C (manufactured by Seiko Epson Corporation), while for the ink set 3, printing was performed using a recording apparatus loaded with an experimental ink jet recording head which could cope with six colors.

(1) Dot diameter

The equivalent circular diameter per dot was measured on 100 samples for the transparent substrate side and the print side (light diffusing, ink-absorptive layer side).

(2) Print density

The reflection density and transmission density on the transparent substrate side were measured with TR-927 (manufactured by Macbeth).

(3) Bleeding

Inks having different colors were used to visually inspect boundaries between colors for bleeding, and the results were evaluated according to the following criteria.

No bleeding with clear boundaries: A
Bleeding with blurred and unclear boundaries: NG

(4) Ink absorption

A blue color (total amount ejected: 30 mg/in.$^2$) prepared from magenta and cyan in an ink amount of 15 mg/in.$^2$) per color was printed as 100% duty. Further, the print density was varied to 90% duty, 70% duty, 60% duty, 50% duty, 40% duty, 30% duty, 20% duty, and 10% duty, and the ink absorption was evaluated in terms of the minimum % duty which caused bleeding or flow of the ink in the print.

(5) Ink permeability

Image data specified in Japanese Standards Association were printed to visually inspect the images for sharpness. Further, light was applied using a light board through the backside of the record to visually inspect the images for sharpness. The results were evaluated according to the following criteria.

Good ink permeation to yield a sharp reproduced image: A
Poor ink permeation to yield an unsharp reproduced image: NG

(6) Ink absorption rate

Printing was performed in an ink amount of 15 mg/in.$^2$ per color to measure the time taken for the ink to be completely absorbed.

(7) Storage stability (storage stability in room)

A print formed by printing an image of a person was allowed to stand in a room in its place not exposed to direct sunlight for three months and then visually inspected for fading. The results were evaluated according to the following criteria.

Not changed from the initial color: A
Faded as compared with the initial color: NG

(8) Ink fixation

A print formed by printing an image of a person was allowed to stand under an environment of 40°C and 85% RH for one week and then visually inspected for fading. The results were evaluated according to the following criteria.

Not changed from the initial color: A
Faded as compared with the initial color: NG

(9) Light transmittance

The light transmittance of the recording medium with no printed image was measured according to the procedure set forth in JIS K 7105.

(10) Brightness

The ISO brightness of the recording medium with no printed image was measured according to the procedure set forth in JIS P 8148.

The results were as summarized in the following tables.

Table 1

| | 1. Dot diameter, μm | 2. Print density | | 3. Bleeding | 4. Ink absorption, % | 5. Ink permeation |
|---|---|---|---|---|---|---|
| | Transparent substrate side/print side | Transmission density | Reflection density | | | |
| Example 1 | 80/90 | 3.3-3.8 | 1.8-2.3 | A | 90 | A |
| Example 2 | 85/90 | 3.4-3.8 | 1.9-2.4 | A | 80 | A |
| Example 3 | 75/90 | 3.1-3.8 | 1.6-2.2 | A | 100 | A |
| Comparative Example 1 | 90/90 | 2.5-2.8 | 1.2-1.5 | NG | 70 | NG |

Table 2

| | 6. Ink absorption rate | 7. Storage stability | 8. Fixation | 9. Transmittance, % | 10. Brightness |
|---|---|---|---|---|---|
| Example 1 | Not more than 1 sec | A | A | 40 | 70 |
| Example 2 | Not more than 1 sec | A | A | 50 | 68 |
| Example 3 | Not more than 1 sec | A | A | 30 | 72 |
| Comparative Example 1 | 2 sec | NG | NG | 35 | 70 |

## Claims

1. A recording medium comprising: a transparent substrate; an ink receptive layer and a light diffusing, ink permeable layer provided in that order on the transparent substrate, said recording medium permitting printing to be performed from the light diffusing, ink permeable layer side and, in addition, the print to be viewed through the transparent substrate,

the diameter of the printed dot viewed through the transparent substrate being smaller than that of the printed dot viewed through the light diffusing, ink permeable layer.

2. The recording medium according to claim 1, wherein the ink receptive layer comprises a polyvinyl acetal resin.

3. The recording medium according to claim 2, wherein the polyvinyl acetal resin has a degree of acetalization of 2 to 20% by mole.

4. The recording medium according to any one of claims 1 to 3, wherein the light diffusing, ink permeable layer comprises a carboxyl-modified polyvinyl alcohol, a colloidal silica, a whitening agent, and a synthetic silica.

5. The recording medium according to any one of claims 1 to 4, wherein the light diffusing, ink permeable layer has a thickness of 15 to 40 μm and the ink receptive layer has a thickness of 3 to 15 μm.

6. The recording medium according to any one of claims 1 to 5, which has a total light transmission of 20 to 80%.

7. The recording medium according to any one of claims 1 to 6, which has a brightness of 50 to 90 as observed from the transparent substrate side.

8. The recording medium according to any one of claims 1 to 7, wherein the transparent substrate on its surface in contact with the ink receptive layer has been subjected to adhesion-imparting treatment.

9. The recording medium according to any one of claims 1 to 8, wherein the transparent substrate on its surface not in contact with the ink receptive layer has been subjected to antistatic treatment.

10. An ink jet recording method comprising the steps of: ejecting droplets of an ink composition; and depositing the ink droplets onto the recording medium according to any one of claims 1 to 9.

11. The ink jet recording method according to claim 10, wherein the ink composition comprises a colorant, an organic solvent, water, and a surfactant.

12. The ink jet recording method according to claim 11, wherein the colorant is a pigment and the surfactant is an anionic surfactant having a polyoxyethylene group.

13. The ink jet recording method according to any one of claims 10 to 12, wherein a yellow ink composition, a magenta ink composition, and a cyan ink composition, and optionally a black ink composition are used as the ink composition

14. The ink jet recording method according to any one of claims 10 to 12, wherein six ink compositions in total of a yellow ink composition, two magenta ink compositions different from each other in color density, two cyan ink compositions different from each other in color density, and a black ink composition are used as the ink composition.

15. A recorded medium comprising an image recorded by the ink jet recording method according to any one claims 10 to 14

16. The recorded meidum according to claim 15, which further comprises a protective layer provided on the light diffusing, ink permeable layer after recording the image.

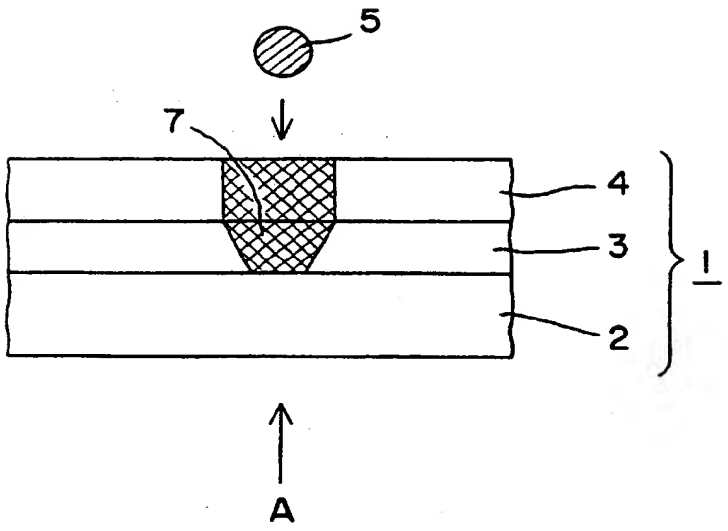



FIG. 1

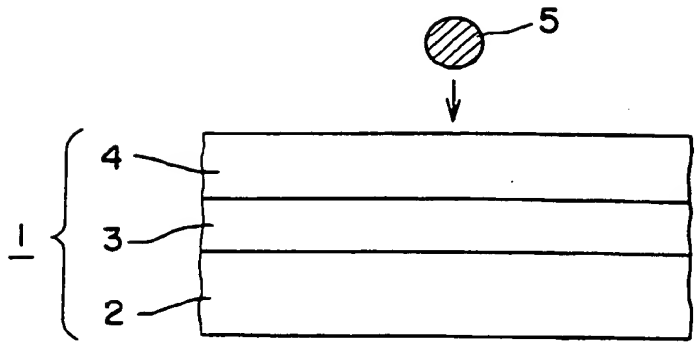



FIG. 2(a)

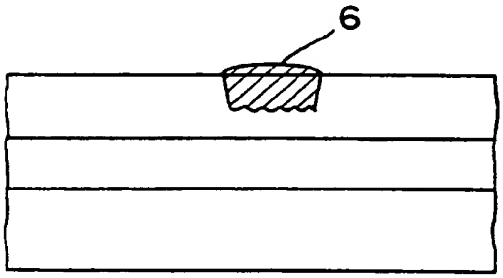



FIG. 2(b)

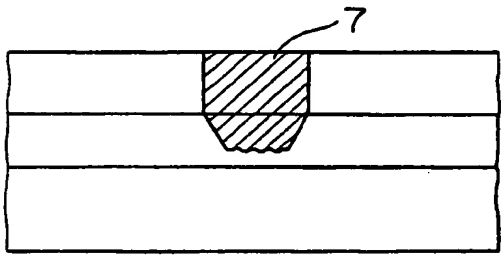



FIG. 2(c)

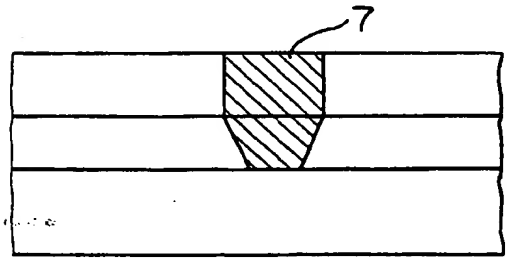



FIG. 2(d)

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number
EP 97 11 9541

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
|---|---|---|---|
| X | EP 0 704 316 A (EASTMAN KODAK COMPANY)<br>* page 3, line 8 - line 17 *<br>* page 4, line 50 - page 5, line 5 *<br>* page 6, line 1 - line 10 *<br>* page 7, line 5 - line 11 *<br>* claims 1-7,18-21 * | 1,5-12, 15 | B41M5/00 |
| X | EP 0 696 516 A (ARKWRIGHT INCORPORATED)<br>* page 2, line 36 - page 3, line 47 *<br>* claims 1-15; examples 1-3 * | 1,5-12, 15 | |
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| X | EP 0 286 427 A (CANON KABUSHIKI KAISHA)<br>* page 3, line 1 - line 26 *<br>* page 3, line 40 - page 4, line 35 *<br>* page 4, line 64 - page 5, line 11 *<br>* claims 1-13; examples 1-6 * | 1,5-12, 15 | TECHNICAL FIELDS SEARCHED (Int.Cl.6)<br>B41M |
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The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 29 January 1998 | Bacon, A |

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Application Number
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| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
|---|---|---|---|
| X | DE 35 23 269 A (CANON KABUSHIKI KAISHA)<br><br>* claims 1-13; figure 1; examples 1-5 *<br>* page 11, line 25 - page 14, line 30 *<br>* page 16, line 1 - page 17, line 15 *<br>* page 19, line 25 - page 20, line 29 * | 1,5-12, 15 | |

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The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 29 January 1998 | Bacon, A |

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